779. *Sorption by* $NH_4{}^+$- *and* Cs^+-*Montmorillonites, and Ion Fixation.*

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The sorptive capacities of samples of $NH_4{}^+$- and Cs^+-montmorillonites for N_2, O_2, A, CH_4, C_6H_6, and H_2O are related to the intersheet spacings of these clays which are intermediate between that for the natural clay and those of the alkylammonium derivatives previously studied.[1,2,3] Certain of the properties exhibited by the $NH_4{}^+$- and Cs^+-clays indicate fixation of these ions on dehydration of the clay, and several observations are made upon the factors controlling cation fixation.

PREVIOUS work here has shown that, whereas only polar sorbates such as water or methanol can penetrate between the sheets of dry Na^+-montmorillonite, many large polar and non-polar sorbates are freely intercalated by alkylammonium montmorillonites.[1-3] Two of the main factors controlling this penetration are the initial sheet

[1] Barrer and MacLeod, *Trans. Faraday Soc.*, 1954, **50**, 980.
[2] *Idem, ibid.*, 1955, **51**, 1290.
[3] Barrer and Reay, *ibid.*, 1957, **53**, 1253.

separation of the outgassed clay and the affinity of the sorbate for the interlamellar surfaces and ions. The alkylammonium clays previously studied have d_{001} spacings ranging from 13·95 Å for the Et_4N^+-clay to 12·0 Å for the $Me·NH_3^+$-form as compared with 9·6 Å for the natural Na^+-clay. To estimate the importance of initial sheet separations intermediate between 9·6 Å and 12·0 Å we have now investigated sorption by NH_4^+- and Cs^+-montmorillonites.

EXPERIMENTAL

(1) *X-Ray and Isotherm Data.*—(a) *Materials.* The ion-exchanged derivatives were formed from the natural clay as previously described [1-3] by treatment with brines of the chloride of the required cation, washing free from excess of salt, and drying from alcohol, acetone, or ether. The purity of the gases used for sorption and the sorption techniques have also been mentioned elsewhere.[1-3]

(b) *X-Ray diffraction.* $Cu-K_\alpha$ radiation, and a flat plate camera 9—11 cm. from the specimen were used. On outgassing NH_4^+- and Cs^+-montmorillonites at 10^{-6} mm. Hg at

FIG. 1. *Cross-section of the cavity formed between two montmorillonite sheets in contact with one another showing the size of various cations in relation to the cavity.*
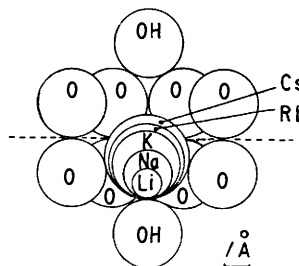
temperatures ranging from 25° to 160°, diffuse first-order lines and irrational series of 001 lines were obtained in the *X*-ray diffraction patterns. This is thought to be due to the ability of the dehydrated cations to sink appreciably into hexagonal holes in the sheet surface.

According to Hofman, Endell, and Wilm's structure,[4] these holes are 3·3 Å in "free diameter," a term denoting that diameter not occupied even by the periphery of the surrounding oxygen atoms. The radius of the oxygen atoms bordering the holes has been taken as 1·4 Å, as has that of the hydroxyl groups.[5] Fig. 1 shows that ions up to 2·4 Å in diameter could sink entirely below the sheet surface. Should the Cs^+ ion, sunk thus in a hole, be directly opposed on the adjacent sheet by a surface oxygen atom, the d_{001} spacing might be expected to be 10·6 Å. Whether Cs^+, of diameter 3·38 Å, would sink to the fullest extent is uncertain. With incomplete "burying" the maximum d_{001} spacing would be even greater than 10·6 Å. If holes on adjacent sheets are opposite one another it should be possible for the lattice to collapse to give a d_{001} spacing of 9·4—9·6 Å. In a turbostratic structure one may therefore expect an irrational series of lines in the *X*-ray diffraction pattern due to the variety of d_{001} spacings from 9·4 Å to >10·6 Å. A similar argument applies to the NH_4^+-clay.

The possibility also exists of the irrational series of lines being due to incomplete exchange by NH_4^+ and Cs^+. Estimation of nitrogen by the Kjeldahl method on a small sample of the NH_4^+-clay gave a content of 60—70 mequiv./100 g. as against 100 mequiv./100 g. of base exchange capacity of the original clay. The NH_4^+-clay was treated only with sodium hydroxide in the nitrogen estimation, and all the nitrogen may not have been released, especially as the clay had been outgassed and some of the NH_4^+ ions may have been fixed in the clay.

Attempted exchange of the Cs^+-clay back to the Na^+-form did not effect any change in the *X*-ray pattern. This again suggests fixation of Cs^+ in montmorillonite. This is not in opposition to the results of Faucher and Thomas,[6] who found a reversible ion-exchange isotherm for K–Cs–K exchange since their material was not outgassed in the Cs^+-form before the exchange back to the K^+-clay.

(c) *Sorption results.* Isotherms for oxygen, argon, nitrogen, and methane at 90° K are shown in Figs. 2 and 3. The sorption is considerable and the isotherms rise sharply up the

[4] Hofmann, Endell, and Wilm, *Z. Krist.*, 1933, **86**, 340.
[5] Barshad, *Proc. Amer. Soil Sci. Soc.*, 1952, **16**, 176.
[6] Faucher and Thomas, *J. Chem. Phys.*, 1954, **22**, 258.

volume axis almost to the v_m value. The v_m values are intermediate between those for the natural clay, where sorption of these gases is limited to external surfaces of the crystallites, and those for organic derivatives such as $MeNH_3^+$- and Me_4N^+-clays where intercalation is known to occur [2,3] (Table 1).

The question arises whether intercalation of the permanent gases and of methane occurs in the NH_4^+- and Cs^+-clays. No expansion beyond that of the outgassed clay being assumed,

FIG. 2. *Isotherms for sorption by* NH_4^+*-montmoril-lonite.* N_2, CH_4, O_2, *and* A *at* 90° K, *and* C_6H_6 *at* 323° K.
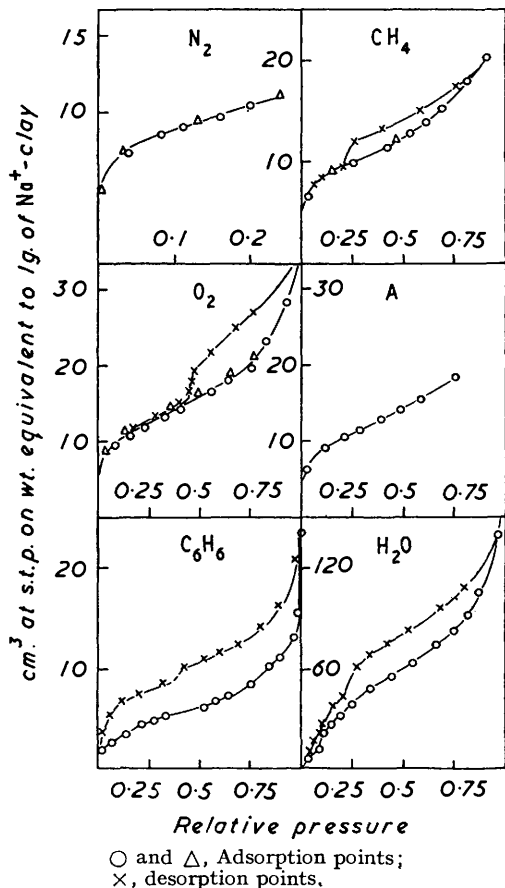

O and △, Adsorption points;
×, desorption points.

FIG. 3. *Isotherms for sorption by* Cs^+*-montmoril-lonite.* O_2, A, *and* N_2 *at* 90° K, *and* C_6H_6 *a* 323° K.

O, Adsorption points; ×, desorption points.
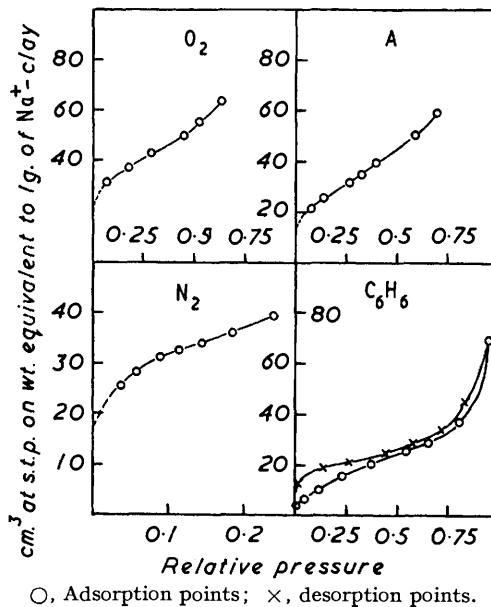
TABLE 1. *Sorption upon* NH_4^+ *and* Cs^+*-montmorillonites compared with the natural clay and the* $Me \cdot NH_3^+$*-form.*

		Clay							
		Natural		NH_4		Cs		$CH_3 \cdot NH_3$	
Sorbate	T (°K)	v_m	A	v_m	A	v_m	A	v_m	A
N_2	90	4·95	21·68	8·92	40·6	30·9	141	43·4	198
O_2	90	5·74	21·88	9·82	37·0	32·2	122	43·9	166
A	90	—	—	8·35	34·6	24·7	103	34·2	142
CH_4	90	—	—	9·99	45·1	—	—	31·3	140
C_6H_6	323	—	—	3·74	38·0	13·0	143	~27	~180 †

* v_m is in c.c. and A in sq.m. on that weight of clay equivalent to 1 g. of Na^+-clay, complete exchange being assumed.

† Since the intercalated benzene molecules have a different orientation with respect to the sheet from those sorbed externally, a different molecular area was used.[2]

there could be intercalation only between some widely separated sheets. In the major part of the clay the interlamellar separation is, from the X-ray study, obviously too low. If additional expansion did occur this would, in accordance with our previous experience,[2,3] be expected to result in irreversibility of the isotherms persisting to low pressures. However, hysteresis at low pressure was not observed with methane, and was noted only to a very slight extent with oxygen, in NH_4^+-montmorillonite (Fig. 2). The slopes of the isotherms above v_m further support the view that there is little intercalation of these gases (Section 3).
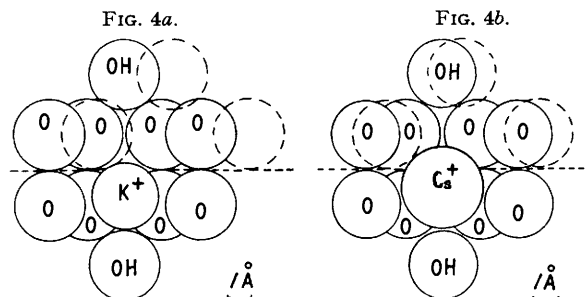
FIG. 4a.   FIG. 4b.

FIG. 4. *Simplified representation of the freedom of superposition of adjacent sheets in K⁺- and Cs⁺-montmorillonites without separation of the sheets. This will affect the proportion of expanded clay in each form.*

In the sorption of benzene at 323° K irreversibility was observed persisting to low pressures (Figs. 2 and 3), and therefore some additional lattice expansion is thought to occur. Nevertheless, the X-ray diffraction patterns for these clays show no substantial shift of the diffuse first-order line in the presence of benzene vapour at relative pressures ranging from 0·06 to ∼1. This indicates that expansion can still involve only a small portion of the clay, presumably that already having a large sheet separation in the outgassed state. That penetration is not complete is also supported by the amounts of benzene sorbed by these clays, as compared with sorption by the alkylammonium forms.[2,3]

Sorption of water on the NH_4^+-clay gives an interesting isotherm (Fig. 2). Adsorption solely upon external surfaces is followed by a small stepwise rise, recalling the intercalation of the first layer in the Na^+-clay,[1] but at a higher relative pressure. No second layer is observed. The X-ray diffraction photograph shows lattice expansion but the lines remain diffuse indicating still that only part of the clay has expanded. The hysteresis loop is of the form previously found where lattice expansion occurs.[1-3]

(2) *External Surface Area and Particle Size of the Cs⁺-Clay.*—Even allowing for a small amount of interlamellar sorption of oxygen, nitrogen, and argon on the Cs^+-clay, the isotherms indicate that the external surface of the Cs^+-form is several times that of the natural form and therefore that particle size must have decreased. A similarly high surface area for Cs^+-montmorillonite was found by Mooney, Kennan, and Wood.[7] The clay derivatives formed here were not ground, and so rupture of the particles normal to the sheets is unlikely to have occurred. Therefore any increase in external surface area on exchange from Na^+ to Cs^+ must be an increase in *sheet* and not *edge* area. Since the total external sheet and edge area of the Na^+-clay is ∼20 m.²/g. and that of the corresponding amount of Cs^+-clay is ∼90 m.²/g., more than 70 m.²/g. of this Cs^+-clay area must be external *sheet* area compared with less than 20 m²/g. on the Na^+-clay. This represents a marked decrease in average particle thickness. All particles being assumed to be of uniform thickness in each case, the decrease in thickness would be from ⩾32 sheets for the Na^+-clay to <8 sheets for the Cs^+-form. It is not thought that there is a general decrease in particle thickness to ∼8 sheets, but rather that some single sheets partly or wholly peel off. Thus if a 30-sheet thick particle exfoliates 4 single sheets, the exposed sheet area is increased fivefold while the average particle thickness is reduced to 6 sheets.

Since individual sheets may be widely separated when in aqueous suspension during ion-exchange,[8] the change in particle thickness may be due to differences in the tendency of the

[7] Mooney, Keenan, and Wood, *J. Amer. Chem. Soc.*, 1952, **74**, 1367.
[8] Norrish, *Discuss. Faraday Soc.*, 1954, **18**, 120.

sheets to coalesce as the gel dries after exchange. This will depend on several factors: (1) charge density of the sheets, which will be approximately constant macroscopically for the sample used throughout this research: (2) the charge on the exchange-ion, again constant in the present experiments; (3) ion size; (4) the liquid from which the gel is dried, *e.g.*, water, methanol, or acetone. Factors (3) and (4) are inter-related. In drying from water the cationic radii are those of the hydrated ions. Thus the screening of charge is greater for the hydrated Na^+ ion than for the Cs^+ ion. One might therefore expect that, if there is complete dispersion of the clay in the ion-exchanging solution, larger crystallites would form from the Cs^+-montmorillonite suspension with consequent decrease in external surface. However, most of the ion-exchanged derivatives formed were dried finally from alcohol, acetone, or ether, and this might cause the formation of small Cs^+-clay aggregates but larger ones of organic forms.

(3) DISCUSSION

(a) *The Significance of the Slope of Isotherms above* v_m.—In many sorption isotherms the portion above the monolayer value v_m is of almost constant slope. In a series of fairly similar sorbents, such as the clays studied here, these slopes may be related to the process of sorption.

On a sorbent where no intercalation occurs, the slope of the isotherm above the v_m value indicates the formation of multilayers and should in some measure be proportional to v_m. This is a simplified picture in which such features as the condensation of sorbates in inter-particle crevices are ignored. Where intercalation does occur and is complete at or near the v_m value (as derived from the B.E.T. equation [9]) the slope of the isotherm will still be proportional to the *external* area of the sorbent. The existence of medium-sized capillaries in which limited multilayer sorption could occur would complicate this situation but will be ignored. If, on the other hand, the calculated v_m is lower than the true monolayer value and intercalation occurs above v_m, then the slope of the isotherm in this region will be greater than that for multilayer formation on the external surface alone.

The series of sorbents studied have external surfaces which are quite similar in character and on which the tendencies to form multilayers of argon or oxygen will be similar. Therefore, in those systems where intercalation is complete at v_m, it should be possible to calculate the external areas, the slope on the Na^+-form where sorption occurs only upon external surfaces being known. It has been suggested, however, that in the sorption of most molecules in the alkylammonium clays intercalation is not complete at the calculated v_m and therefore calculation of external area has not been possible by this means.[3] Nonetheless by applying these criteria it is still possible to differentiate between cases of purely external sorption and partly internal, partly external sorption.

If we express sorption in the region above v_m by the empirical expression $v - v_m = kAp$, where A is the surface sorbing above v_m, then $\delta v/\delta p = kA$. Then for sorption which is solely external $\delta v/\delta p \propto v_m$. This will not hold where intercalation occurs. Table 2

TABLE 2.

Clay derivative	Sorption of O_2 at 90° K			Sorption of A at 90° K		
	$\dfrac{\delta v}{\delta p}$	v_m	$v_m/(\delta v/\delta p)$	$\dfrac{\delta v}{\delta p}$	v_m	$v_m/(\delta v/\delta p)$
Na^+	0·5	0·58	1·16	—	—	—
NH_4^+ *	1·0	1·0	1·0	1·0	1·0	1·0
Cs^+	4·1	3·3	0·8	3·4	3·0	0·89
$MeNH_3^+$	2·0	4·5	2·25	1·8	4·1	2·3
$Me_2NH_2^+$	0·8	3·8	4·75	1·0	4·2	4·2
Me_3NH^+	1·0	3·7	3·7	1·0	4·2	4·2
Me_4N^+	1·6	4·3	2·7	1·9	4·4	2·3

* v_m and $\delta v/\delta p$ have been taken arbitrarily as 1·0 for the NH_4^+-clay.

summarises relevant data and suggests that the conditions of sorption do not differ markedly on the Na^+-, NH_4^+-, and Cs^+-clays. Since it was earlier established that there

is no intercalation of oxygen or argon in the Na^+-clay, this appears to be largely true for the NH_4^+- and Cs^+-forms. On the other hand, for the organic clays where intercalation occurs the values of $v_m/(\delta v/\delta p)$ are all substantially greater than unity.

(b) *Ion Fixation.*—We have given as one reason for the diffuse d_{001} lines obtained in the X-ray diffraction photos of NH_3^+- and Cs^+-montmorillonites the sinking of these ions into the hexagonal holes in the sheet surfaces with the varying degrees of lattice shrinkage which this permits in a structure of randomly superposed sheets. While benzene is intercalated by both clays (Section 1, c) the quantity sorbed is only a fraction of that which is sorbed when the interlamellar area is freely available for sorption.[2,3] This is supported by the X-ray diffraction photographs of the benzene–clay systems which do not differ appreciably from those of the outgassed clays. Again, in the sorption of water on NH_4^+-montmorillonites, although there is a shift of the d_{001} line in the X-ray pattern the line remains diffuse and the interlamellar spacing lower than expected if general swelling occurred. Finally, no change in the X-ray pattern occurs when we attempt to re-exchange to the Na^+-form a sample of Cs^+-montmorillonite which has been outgassed.

These observations may indicate " fixation " of NH_4^+ and Cs^+ ions in montmorillonite after outgassing even at room temperature. Fixation of these ions has been noted else-where.[5,10,11] However, when the published investigations of fixation of the alkali and

TABLE 3.

Cation	r(Å) [17]	Estimates of fixation *					
		1	2	3	4	5	6
Li⁺	0·60	<20% Fixation	N.f.	F.	—	F.	F.
Mg⁺⁺	0·65	30%	,,	,,	—	,,	—
Na⁺	0·95	20%	,,	N.f.	N.f.	—	—
Ca⁺⁺	0·99	<20%	,,	,,	F.	—	—
Sr⁺⁺	1·13	28%	,,	,,	—	N.f.	—
K⁺	1·33	55%	F.	,,	—	—	—
Ba⁺⁺	1·35	45%	N.f.	,,	—	N.f.	—
NH₄⁺	1·48	50%	,,	—	—	—	—
Rb⁺	1·48	50%	F.	,,	—	—	—
Cs⁺	1·69	42%	N.f.	,,	—	—	—

* F. = fixation; N.f. = no fixation.

Conditions of fixation.

1. Miami loam (essentially montmorillonite) dried at 100°, rehydrated for 24 hr., then exchanged with HCl: results not absolute.[10]

2. Montmorillonite dried at 105° then exchanged with NH_4OAc; alternatively dried and swelling with glycerol measured, in which case only K^+ appeared to be fixed.[12]

3. Montmorillonite heated to 100°, 200°, 330°, 430°, 540°, and 640°, then soaked in glycerol and X-rayed. Li^+ and Mg^{++} fixed after heating to 330°. The other ions were not fixed after heating to 430°.[13]

4. Change in hydration of Ca^{++} clay after heating to 350°.[14]

5. Samples heated to 100°, 200°, 300°, etc., then rehydrated, and the dehydration–temperature curve determined gravimetrically.[15]

6. Li^+-montmorillonite air-dried at 125° no longer swells in water.[16]

alkaline-earth cations in montmorillonite and related minerals are compared with the theories put forward to explain them, there appears to be little agreement. Table 3 summarises some of this work. The main reasons for this disagreement must be that

[9] Brunauer, Emmett, and Teller, *J. Amer. Chem. Soc.*, 1938, **60**, 309.
[10] Page and Baver, *Proc. Amer. Soil Sci. Soc.*, 1940, **4**, 150.
[11] van der Marel, *Soil Sci.*, 1954, **78**, 163.
[12] Wear and White, *ibid.*, 1951, **71**, 1.
[13] Greene-Kelly, *Clay Minerals Bull.*, 1952, **1**, 221; 1953, **2**, 52.
[14] Mering, *Trans. Faraday Soc.*, 1946, **42**, B, 205.
[15] Garcia, *Anales real. Soc. españ. Fis. Quím.*, 1949, **45**, B, 1183; 1951, **47**, B, 357.
[16] Hofmann and Klemen, *Z. anorg. Chem.*, 1950, **262**, 95.
[17] Pauling, " The Nature of the Chemical Bond," Cornell, 1940.

different clay samples have been used and that differing conditions of ion fixation and several methods of measuring fixation have been employed.

Differences in ion fixation appear to depend upon factors which come under two general headings.

(i) Properties of the clay mineral affecting all the cationic forms. These include the charge density of the clay sheets, its distribution between octahedral and tetrahedral layers, and the size of the platelets. The exact nature of these effects is uncertain. The interaction of the penetrating sorbate with the aluminosilicate sheets will also be important.

(ii) Factors differing in the various cationic forms: (*a*) Effective cation radius; this will depend upon the conditions of drying the clay, *e.g.*, low-temperature drying may account for those cases where Li^+ and Mg^{++} have been found not to be fixed. The radius of the cation will control its ability to sink into the haxagonal holes in the sheet surface (Fig. 1). This is turn gives rise to differences in the balance between other factors. (*b*) The electrostatic bonding of the ion with the sheets. (*c*) The energy of interaction of the cation with the penetrating sorbate. (*d*) The intersheet spacing of the dehydrated clay which affects the amount of lattice expansion required for penetration.

As the radius of the ion increases it will sink less deeply into the holes in the sheet surface and thus come less close to the main seat of negative charge in the octahedral layer so that there is a decrease in the electrostatic bonding of the ion to the sheet. Up to Sr^{++}, with ions sunk in only one sheet, it will be possible for the clay to collapse completely to give the minimum d_{001} spacing no matter how the sheets are oriented laterally. Above this radius a proportion of the clay will have a d_{001} spacing greater than the minimum. If we assume a constant degree of randomness of lateral orientation of the sheets in the various cationic forms then incompleteness of lattice collapse will increase with increasing ion diameter above 2·4 Å, the depth of the holes (Fig. 4). This in turn affects the amount of additional lattice expansion required for penetration by the sorbate. Then the energy of interaction of ion with sorbate will fall from Li^+ to Cs^+ as radius increases and will also vary with cation charge. The balance of this energy term with those associated with the factors mentioned previously will vary from one sorbate to another. Thus an ion might be fixed with respect to glycerol but not to water. These seem to be some of the most important factors involved. Others, such as the steric suitability of certain cations for co-ordination with the oxygen atoms of the clay sheets, have been dealt with elsewhere.[12] It can be concluded that complete understanding of cation fixation requires more extensive experimental work than has yet been carried out.